MAGNETIC RESONANCE STUDIES OF LABELED GUEST MOLECULES IN COAL

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We have used magnetic resonance techniques to probe the time scales of motion for a series of labeled guest molecules imbibed in subbituminous Wyodak and bituminous Illinois #6 coals. Nuclear magnetic resonance (NMR) was used to study a suite of such guests which were either deuterated or fluorinated, while electron spin resonance (ESR) was used to examine paramagnetic TEMPOL spin labels. These labeled guest molecules can be observed directly with a minimum amount of interference from the nuclei and paramagnetic species naturally occurring in the coal. By choosing a variety of differently labeled species, a broad range of time scales for molecular motion can be examined. The rate and nature of the motion provides information about the environment of the guests in the coal structure.

Dry coal samples (10-20 mesh) were exposed to various solvent vapors while contained in closed jars. The solvent uptake was monitored by periodic weighing of the sample during the exposure period. As shown for C_6H_6 and C_5H_5N in Illinois #6 coal (Figure 1), the uptake pattern depends upon the choice of solvents: benzene uptake approaches an asymptotic value in roughly one week while pyridine continues to be included over a much longer time period. The amounts of imbibed labeled molecules in the coals used for the present study, shown in Table 1, range from $\sim$0.1-$\sim$10 m mole of solvent/gm of coal.

In most liquids, rapid molecular motion causes averaging of the interactions between nuclear and electronic spins and their environment. If the rate of motion becomes sufficiently slow, these interactions are no longer averaged and a change in the magnetic resonance signal, typically a broadening, is observed. This averaging process has been studied in many liquids and solids and relatively simple theories have been developed which predict the characteristic times for motion required for the onset of averaging for different electronic and nuclear spins (1). For example, in 2-fluoropyridine the ^{19}F NMR is broadened by dipolar interactions, principally with protons on the same molecule, and motion on a time scale shorter than 250 μ sec is needed to average the interaction. For the $-CF_3$ components of hexafluoropropanediamine, this characteristic time is $\sim$100 μ sec. The ^2H nuclei in deuterated labels are broadened by the stronger nuclear electric quadrupolar interaction and more rapid motion ($\sim$5 μ sec) is required for averaging. Interactions of the much larger electronic moments in the paramagnetic TEMPOL spin labels require times on the order of 10^{-8} sec to be averaged. A combination of these labels allows us to survey rates of motion which vary by over a factor of one million.

The derivative of the ^{19}F NMR absorbtion of 2-fluoropyridine in Illinois #6 coal is shown in Figure 2. A narrow NMR line is seen at 300K, with no evidence for the broad component which would indicate molecules moving more slowly than 250 μ sec. No broad ^2H NMR line is seen in coal samples containing D_2O. However both broad and narrow components are seen in coals with C_6D_6 and C_5D_5N guests. The derivative of the ^2H NMR for C_6D_6 in Illinois #6 is shown in Figure 3. The same data is displayed at two levels of gain to show the two satellites which occur on either side of the intense central component. Very roughly, comparable numbers of nuclei contribute to the narrow and broad components. The C_6D_6 molecules contributing to the central absorbtion are moving on time scales shorter than 5 μ sec and the ^2H quadrupole interaction is completely narrowed. The satellite splitting for the broad C_5D_5N component is twice as large as in the C_6D_6 case. From the magnitudes of these broad spectra (2) we infer that the C_6D_6 molecules are still spinning about their C_6 symmetry axis at times shorter than 5 μ sec, while the C_5D_5N molecules are not. The restricted motion of this class of C_6D_6 molecules suggests that they may be sterically confined by the nearby coal matrix. The absence of rapid motion for this class of C_5D_5N molecules may reflect a chemical interaction between the molecules and the coal matrix.

ESR studies of the TEMPOL spin label also show this slowing down process in the coal. Immediately after adding a TEMPOL solution to a coal sample, a narrow triplet ESR signal from the TEMPOL in the liquid is super-imposed on the carbon radical signal in the coal (Figure 4A). The narrow TEMPOL lines broaden as time passes while the total EPR signal does not change, again implying the loss of averaging due to slower motion of the molecules (Figure 4B). The characteristic time of motion is therefore longer than 2×10^{-8} sec. The reduction of the narrow triplet signal intensity (Figure 4C) is proportional to $\exp(-\alpha t^{1/2})$ suggesting that this slowing of the motion reflects diffusion of the TEMPOL labels into the coal.

Pulsed NMR studies of the narrow component of the resonance line also show the change in motion of a molecule when introduced into the coal solid. The energy exchange between ^{19}F nuclei in 2-fluorophenol and their environment was determined in the free liquid and for molecules included in coal by using spin lattice relaxation (T_1) measurements. T_1 is frequency independent for both systems, but the relaxation time is much shorter for the guest molecules in coal: $T_1 = 13 \pm 3$ m sec, in comparison with $T_1 = 1.5 \pm 0.3$ sec for the free liquid at the same temperature (300K). These data imply characteristic times of motion for the guest species. A factor of 100 slower than for the free species.

In summary, a combination of labeled molecular probes and different observation techniques provides information on the environment and motion of molecular species in coal. The range of characteristic times of motion is indicated schematically in Figure 5. As illustrated in the case of the spinning C_6D_6 molecules, the type of the motion may also be deduced in some cases.

REFERENCES

1. This averaging phenomenon is discussed by A. Abragam, "Principles of Nuclear Magnetism" (Oxford, 1961), Chapter X.

2. See R. G. Barnes in "Advances in Nuclear Quadrupole Resonance", J. A. S. Smith, Ed. (Heydon and Sons, London, 1974), v. 1, p. 235 ff.

TABLE 1: MOLECULAR UPTAKE DURING THE SWELLING PROCESS

Coal Type	Imbibing Molecule	Millimoles Imbibed/Gram of Coal
Wyodak:	D_2O	8.49
	C_5D_5N	8.93
	C_6D_6	1.26
Illinois #6:	D_2O	5.79
	C_5D_5N	6.21
	C_6D_6	2.08
	2-Fluorophenol	4.83
	4-Fluorophenol	1.88
	2-Fluoropyridine	6.09
	C_6F_6	0.47
	Hexafluoro Propane Diamine	0.29

Figure 1: Examples of the Swelling Process:

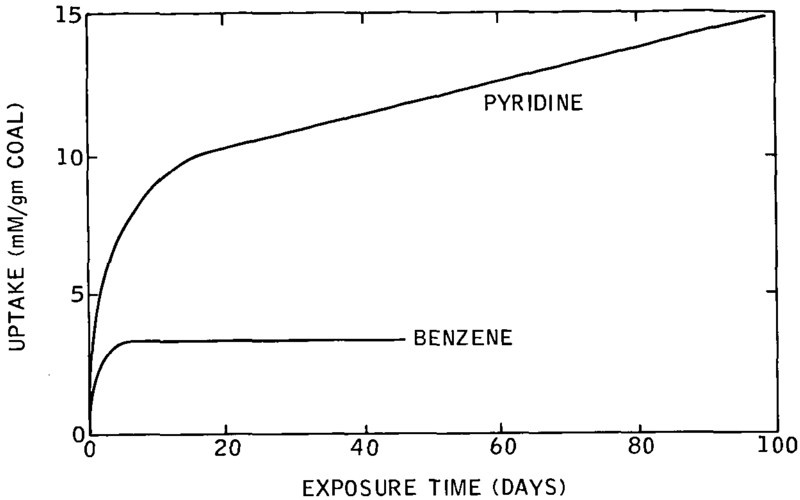


Figure 2: The ^{19}F NMR of Illinois #6 Coal swelled with 2-fluoropyridine shows only a narrow component.

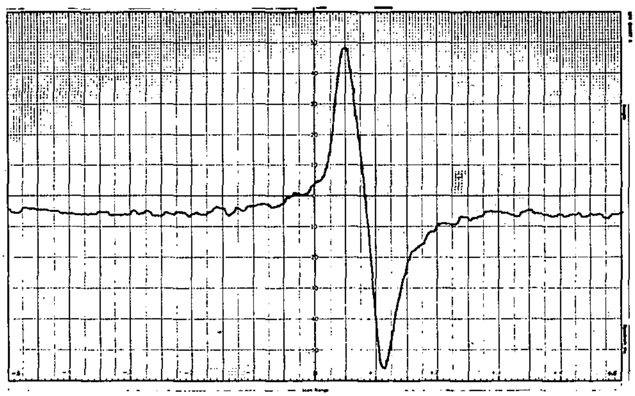
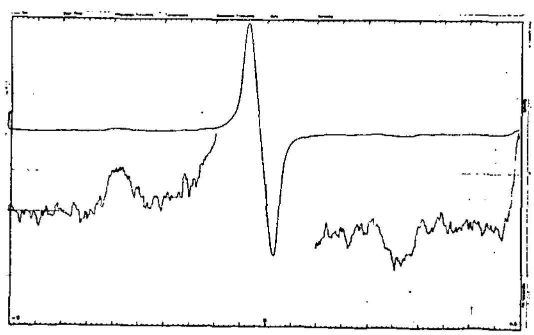


Figure 3: Both narrow and broad ^{2}D NMR signals are observed in Illinois #6 coal swelled with C_6D_6.



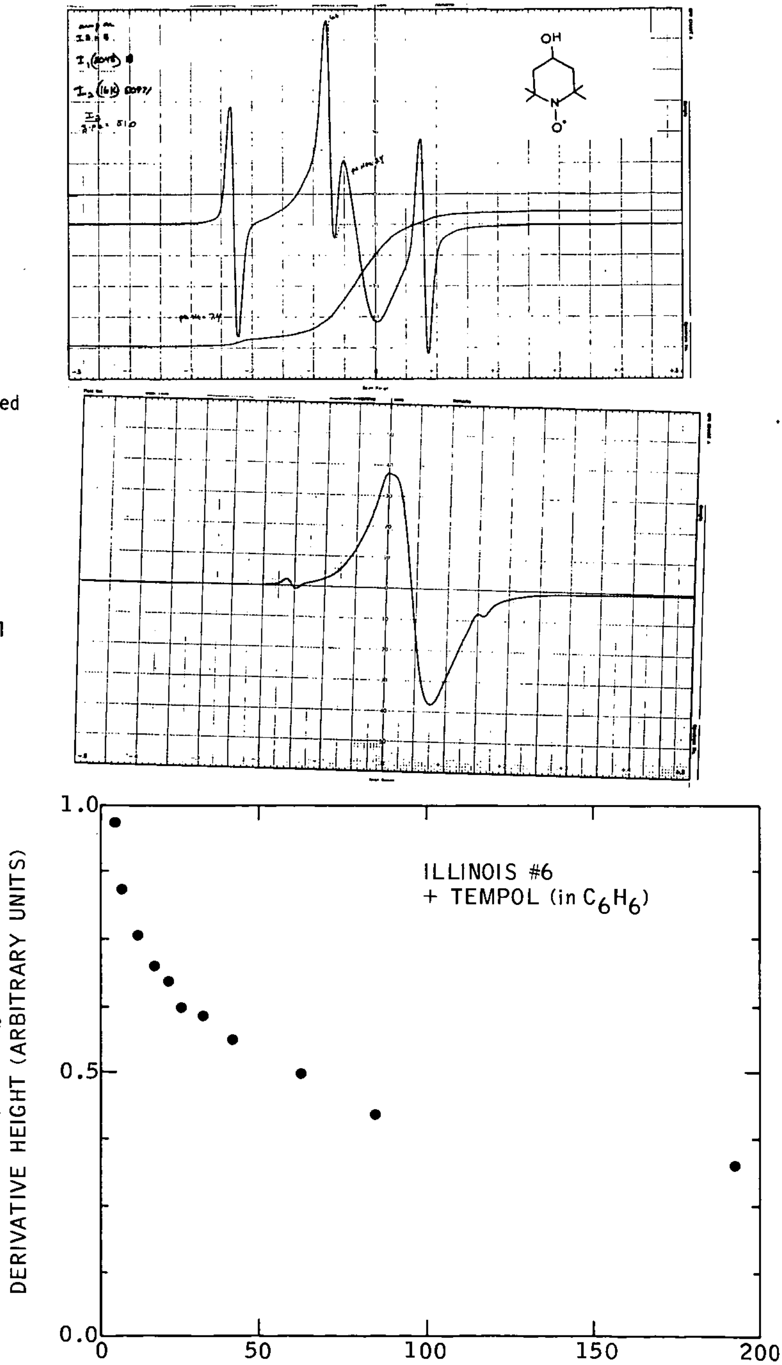


Figure 4: Coal Swelling with a paramagnetic spin label (TEMPOL)

A. Upon initial exposure of TEMPOL to coal, the narrow spin label triplet signal is superimposed upon the carbon radical signal from the coal.

B. At long times, only a trace of the triplet TEMPOL signal remains.

C. An example of the loss of TEMPOL signal intensity with time for Illinois #6 coal exposed to a solution of TEMPOL in benzene.

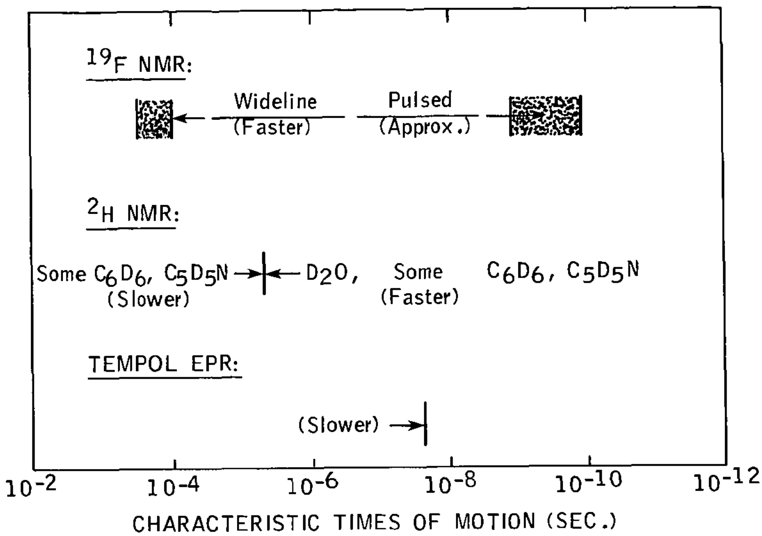


Figure 5: A survey of characteristic times of motion probed by the current labeled molecules.